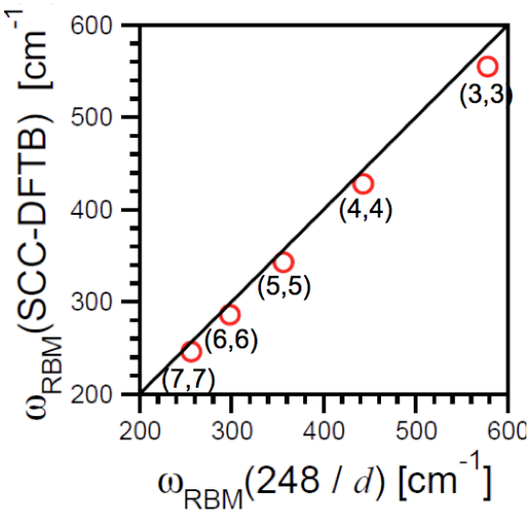
First Principles-Based Estimate of the Critical SWCNT Length for Raman D and G Band Intensity Inversion

Yoshifumi Nishimura,[1] Henryk A. Witek,[2] Stephan Irle[1]
[1]*Department of Chemistry, Nagoya University Nagoya 464-8602, Japan*
[2]*Department of Applied Chemistry, National Chiao Tung University, 30010 Hsinchu, Taiwan*

We present Raman spectra of finite-length, hydrogen-terminated single-walled carbon nanotube (SWCNTs) model systems with up to ~1000 atoms on the basis of an approximate density functional theory (DFT), namely the self-consistent-charge density-functional tight-binding method (SCC-DFTB) [1]. Using our implementation of analytical second-order geometrical derivatives [2] and specifically developed parameter sets, it is possible to accurately compute vibrational frequencies and IR and Raman intensities of fullerenes [3] and nanodiamonds [4]. Here, we present our first study of SWCNT molecular models with different lengths and diameter.



A comparison of the DFTB-predicted Raman spectra for the smallest SWCNT systems with those from standard DFT indicates excellent performance of the approximate tight-binding method, as was also reported earlier [3]. In order to identify Raman intensities of bands originating from CH vibrational modes, we employed the technique of hydrogen mass rescaling.

Simulations of Raman spectra of (*n*,*n*) SWCNTs with *n* = 3 to 7 at a fixed length of 8 nm (largest model: $C_{924}H_{28}$) confirm the previously found quantitative inverse relationship between tube diameter and radial breathing mode frequency [5] (see Fig. 1).

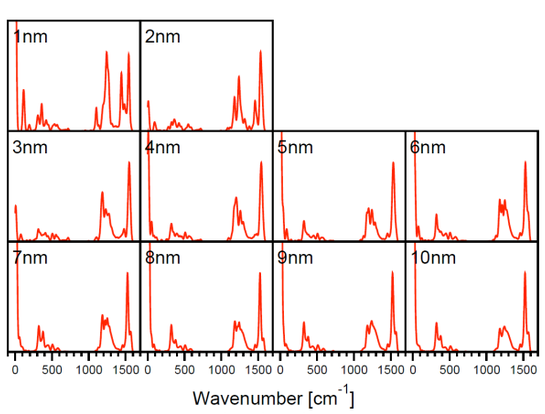


Figure 2. DFTB-simulated Raman spectra of hydrogen-terminated (5,4) SWCNTs with increasing tube length, from 1 to 10 nm.

As model systems in the study of the length-dependence of Raman intensities, we employed hydrogen-terminated (5,4) SWCNTs with lengths ranging from 1 to 10 nm, *i.e.* $C_{80}H_{18}$ to $C_{740}H_{18}$. Our results indicate that the critical SWCNT length for Raman D to G band intensity inversion is already around 1 nm (see Fig. 2).

In our presentation, we will also discuss theoretical IR spectra, vibrational density of states, electronic density of states, and HOMO-LUMO gaps of the various SWCNT molecular models, and discuss the size evolution of these quantities to the corresponding bulk properties.

[1] M. Elstner, D. Porezag, G. Jungnickel, J. Elstner, M. Haugk, Th. Frauenheim, S. Suhai, G. Seifert, *Phys. Rev. B,* **58**, 7260 (1998).
[2] H. A. Witek, S. Irle, K. Morokuma, *J. Chem. Phys.* **121**, 5163 (2004).
[3] H. A. Witek, S. Irle, G. Zheng, W. A. de Jong, K. Morokuma, *J. Chem. Phys.*, **125**, 214706 (2006).
[4] W. Li, S. Irle, H. A. Witek, *ACS Nano*, **4**, 447 (2010).
[5] A. Jorio *et al.*, *Phys. Rev. Lett.,* **86**, 1118 (2001).